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# Poly(internal olefins)

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## I. INTRODUCTION

Synthetic hydrocarbons, esters, and hydroisomerized or hydrocracked base stocks, the latter commonly classified as nonconventional base oils (NCBOs), are widely used to formulate multigrade, low viscosity, top tier engine oils suitable for modern vehicles. Furthermore, they are increasingly used in the field of high quality industrial lubricants. AgipPetroli and EniChem Augusta have developed a new synthetic component, poly(internal olefin) (PIO), with a proprietary process that uses *n*-olefins as feedstock.* This new component is an excellent base oil for the formulation of high performance engine and industrial lubricants.

This chapter describes the manufacturing process, the physical and chemical properties, and the performance of poly(internal olefins) in semi- or fully synthetic multigrade engine oils and synthetic industrial oils. Comparison with poly(α-olefins) (PAOs) is included.

There are two main reasons for replacing conventional base stocks in part or completely with synthetics or with NCBOs:

1. These products lower volatility and improve rheological behavior, particularly at low temperatures.
2. They improve performance of finished products by virtue of this superior thermo-oxidative behavior and lower tendency to form deposits [1].

* At the time of development of PIO, AgipPetroli and EniChem Augusta were both units of the ENI Group, the major Italian oil company. EniChem Augusta was subsequently acquired by RWE DEA Group under the name of Condea Augusta.



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Synthetics and NCBO widely differ in properties, levels of performance, additive response, and, last but not least, cost; the problem associated with their use in lubricants is, therefore, the optimization of the cost/performance ratio.

Oil manufacturers have developed and are using different solutions depending on availability of components, type of lubricant, and market strategy; PIOs represent a potential alternative.

PIOs were evaluated in comparison to PAOs because the latter are the best known and most widely used hydrocarbon-type synthetic base stocks. Moreover, a large amount of data is already available from the development of commercially available additive technologies.

Additional data must be accumulated before NCBOs can be properly compared with PAOs. We nevertheless point out that in the field of hydrocracked base stocks in particular, different levels in terms of price, physico chemical characteristics, performance and quality consistency have been reported.

## II. MANUFACTURING

PIOs are long chain hydrocarbons, typically a linear backbone with some branching randomly attached; they are obtained by oligomerization of internal *n*-olefins, (Structural details based on unpublished data from mass spectroscopic studies: desorption chemical ionization, desorption electron impact, $^{1}H$ NMR, and $^{13}C$ NMR.) The catalyst is $BF_3$ complexed with a proton source that leads to a cationic polymerization [2]. This system was chosen for the easy removal of $BF_3$ from reaction and because the cycle time is shorter than those of other polymerization reactions (free radical, Ziegler type, etc.) [3–5].

The process consists of four steps (Fig. 1):

reaction
neutralization/washing
hydrogenation
distillation

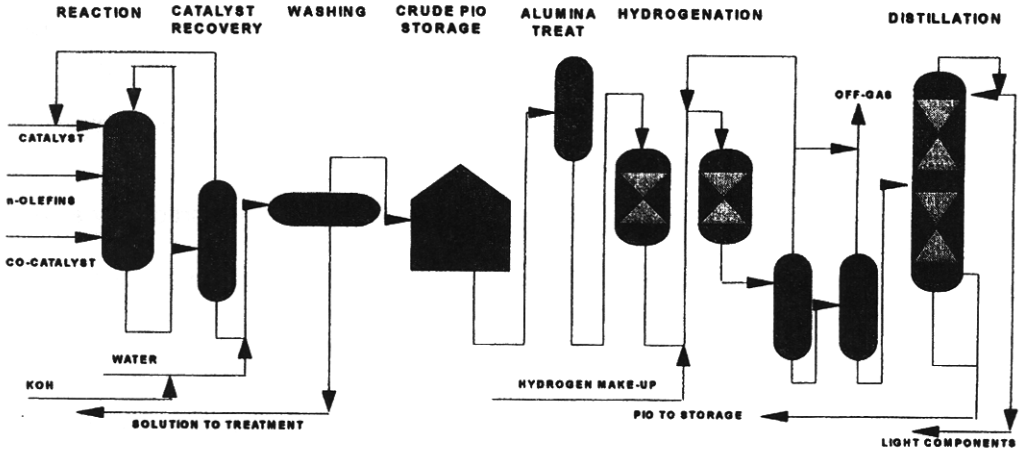


**Figure 1** Plant flow sheet for PIO production.

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### A. Reaction Step

Internal olefins ($C_{15}$–$C_{16}$ blend, at an 80/20 ratio) and catalyst ($BF_3$ and proton source) are fed continuously in loop reactors; the reactors are under $BF_3$ pressure control, and at the end of the reaction, $BF_3$ is stripped and recycled.

### B. Neutralization Step

The reaction product is neutralized with an alkaline solution. Then the heavy phase containing boron and fluorine salts is removed and sent to waste treatment, while the light phase (crude PIO) is sent to storage for further processing.

### C. Hydrogenation Step

Before hydrogenation, the crude PIO is treated over alumina beds to remove all organic fluorine; this treatment is necessary both to avoid poisoning of the hydrogenation catalyst and to prevent possible stress corrosion in the hydrogenation unit.

### D. Distillation Step

The hydrogenated product is distilled to remove all short paraffins, isoparaffins (by-products of the reaction), and light ends. The bottom product (finished PIO) is sent to storage. Typical yield in PIO is more than 85% based on feedstock. By distillation, the 6 cSt product can be split in 4 and 8 cSt cuts.

## III. ANALYSIS AND CHARACTERISTICS

Table 1 summarizes the main physicochemical characteristics of PIOs and PAOs. To ensure meaningful comparisons, data were generated in the same laboratory. Evaluation of high perfor-

**Table 1** Polyolefin Characteristics

| | Viscosity cuts | | | | | |
|---|---|---|---|---|---|---|
| | 4 cSt | | 6 cSt | | 8 cSt | |
| Characteristic | PIO | PAO | PIO | PAO | PIO | PAO |
| Composition | | | | | | |
| HPLC composition, % mass | | | | | | |
| Dimers | 100 | — | 66 | — | 40.5 | — |
| Trimers | Traces | 85 | 34 | 30 | 59.5 | 9 |
| Tetramers | — | 15 | — | 47 | — | 56 |
| Higher | — | — | — | 23 | — | 35 |
| NMR $CH_2/CH_3$ ratio | 4.8 | 5.1 | 4.9 | 5.5 | 5.1 | 5.4 |
| Physico chemical characteristics | | | | | | |
| Viscosity at 100°C, cSt | 4.33 | 3.84 | 5.66 | 5.83 | 7.72 | 7.71 |
| Viscosity at 40°C, cSt | 20.35 | 16.7 | 30.4 | 30.5 | 48.2 | 45.8 |
| VI | 122 | 124 | 128 | 137 | 127 | 137 |
| Viscosity at −25°C, cP | 750 | — | 1550 | 1500 | 3300 | 2800 |
| Viscosity at −30°C, cP | 1150 | 850 | 2500 | 2300 | | |
| Pour point, °C | −51 | −64 | −48 | <−51 | −45 | <−51 |
| Flash point, °C | 230 | 229 | 234 | 235 | 254 | 260 |
| NOACK, % wt loss | 15.3 | 15.2 | 9.0 | 7.8 | 5.6 | 4.1 |

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**Table 2** Thermo-Oxidative Performances and Deposit-Forming Tendency[a]

| Test description | Source | Evaluation conditions |
|---|---|---|
| IP 48 MOT/E | In-house test | Gives information about oxidative oil thickening. Oil containing metal catalyst is oxidized at high temperature under airflow. |
| Microcoking test | GFC L 27T94 | Evaluates the deposit-forming tendency. A small oil sample is put on a hot aluminum plate with a temperature gradient for 90 min; a merit rating (10 = clean) is given. |

| | Viscosity cut 6 cSt | |
|---|---|---|
| Test Results | PIO | PAO |
| IP 48 MOT/E | | |
| 170°C, 100 ppm Fe, 48 h | | |
| Viscosity increase at 40°C, % | 157 | 153 |
| Total acid number, mg KOH/g | 7.2 | 7.5 |
| IR at 1720 $cm^{-1}$ A/cm | 185 | 186 |
| IR at 1630 $cm^{-1}$ A/cm | 20 | 18 |
| Microcoking Test: temperature gradient 230–280°C | | |
| Zone A merit | 7.6 | 7.7 |
| Zone B merit | 9.0 | 8.8 |
| Merit average | 8.3 | 8.3 |

[a] Abbreviations as follows: GFC, Groupement François de Coordination (French national body in TAN, total acid number; IR, infrared absorption.

mance liquid chromatographic (HPLC) data on PIOs and PAOs reflects the differences in the feedstock used in their production: *n*-olefin $C_{15}$–$C_{16}$ for PIO, $\alpha$-$C_{10}$ for PAO. The differences in the chain length and in the double-bond position influence the branching, as can be seen from NMR data.

Table 2 reports the thermo-oxidative performance and the related deposit-forming tendencies, as evaluated in bench tests: the thermal and oxidation stability the microcoking test (MCT) and IP 48 modified oxidation test/Euron (MOT/E) is excellent—and equivalent to values for PAOs in these tests.

Table 3 reports the tribological behavior as measured in standard rig tests of the American Society for Testing and Materials (ASTM): PIOs perform somewhat better in the wear test.

**Table 3** Tribology

| | 6 cSt base stock | |
|---|---|---|
| Test | PIO | PAO |
| Four-ball EP test: ASTM D-2783 | | |
| Seizure load, kg | 40 | 40 |
| Welding load, kg | 120 | 100 |
| Four-ball wear test: ASTM D-4172 | | |
| Wear scar diameter, mm | 0.66 | 1.18 |

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# IV. APPLICATIONS

## A. Automotive Engine Oils

Engine oil formulation is the main field in which PIOs can find their preferred field of application. This is because synthetic base stocks or NCBOs are needed to meet the current, more stringent requirements for finished lubricants from original equipment manufacturers (OEMs) and from European automakers (ACEA: Association des Constructeurs Européens d'Automobiles).

AgipPetroli has collected an extensive series of data in order to assess PIO performance in this respect. More data are expected to be collected as well, as fallout from new formulations being developed.

The evaluation project has been addressed in four main areas:

1. To compare part synthetic 10W-40 formulations employing PAOs versus the same formulation containing PIOs.
2. To compare fully synthetic formulations employing PAOs with the same formulation containing PIOs.
3. To assess the absolute performance of fully synthetic formulations employing PIOs.
4. To compare fully synthetic formulations employing PAOs with a 30% PAOs replaced by PIOs.

The rationale was to gain performance evidence, taking primarily into account the opportunities and constraints set by the current Base Oil Interchange Guidelines (BOIG) of API Engine Oil Licensing and Certification System (EOLCS) and Association Technique de 1'Industrie European des lubricants European Engine lubricant Quality Monitoring System (ATIEL EELQMS).

According to the latter, PIOs are to be classified as a "Group III" base stock, whereas PAOs constitute a specific "Group IV" base stock.

### 1. Part Synthetic 10W-40s Constitute One of the Most Widespread Grades on the European Market

An extensive series of blending tests was performed, using additive technologies from different sources with top performance credentials. Some significant data are given in Table 4. Rheology

**Table 4** 10W-40 Part Synthetic Engine Oils Commercial Additive Technology[a]

| | Oil 1 | Oil 2 | Oil 3 | Oil 4 | Oil 5 | Oil 6 |
|---|---|---|---|---|---|---|
| PIO 4 cSt, % mass | 14.0 | | 14.0 | | | |
| PAO 4 cSt, % mass | | 12.0 | | 12.0 | | |
| PIO 6 cSt, % mass | | | | | 23.0 | |
| PAO 6 cSt, % mass | | | | | | 23.0 |
| Mineral base stock, % mass | 62.9 | 64.9 | 62.9 | 64.9 | 54.4 | 54.4 |
| Package code | A | A | B | B | C | C |
| % mass | 13.0 | 13.0 | 13.0 | 13.0 | 13.0 | 13.0 |
| VII (n/d OCP) % mass | 9.7 | 9.7 | 9.7 | 9.7 | 9.2 | 9.2 |
| PPD, % mass | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Viscosity at 100°C, cSt | 13.94 | 13.99 | 13.98 | 13.92 | 14.08 | 14.05 |
| Viscosity at −20°C, cP | 3350 | 3350 | 3350 | 3350 | 3300 | 3300 |
| Viscosity index | 153 | 156 | 153 | 152 | 145 | 147 |
| NOACK, % mass | 10.9 | 11.2 | 11.0 | 11.2 | 10.4 | 9.8 |

[a] Abbreviations as follows: OCP, olefin co-polymer; PPD, pour point depressant.

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**Table 5** SH Test Program Formulations and Typical Inspections

| | Oil A | Oil B |
|---|---|---|
| 150 Solvent neutral | 47.2 | 47.2 |
| PAO 6 cSt | 27.0 | — |
| PIO 6 cSt | — | 27.0 |
| Ester | 3.0 | 3.0 |
| Package | 12.8 | 12.8 |
| VI improver | 10.0 | 10.0 |
| Viscosity at 100°C, cSt | 15.4 | 15.3 |
| Viscosity at 40°C, cSt | 92.7 | 94.2 |
| VI | 176 | 172 |
| Viscosity at −20°C, cP | 3150 | 3300 |
| Borderline pumping temperature (BPT), °C | −25 | −25 |
| Pour point, °C | −45 | −42 |
| Viscosity at 150°C, cP at $10^6$ $s^{-1}$ | 4.1 | 4.2 |
| Total base number (TBN), mg KOH/g | 7.9 | 7.9 |
| Sulfated ash, % mass | 1.2 | 1.2 |
| NOACK volatility, % mass | 10.0 | 10.0 |

and volatility are usually to meet the ACEA limits (with possibly a more severe limit of 12% wt loss for the NOACK volatility, as set by one OEM). Optimization calls for keeping the synthetic (or non-conventional) base oil and viscosity index improver (VII) content to a minimum to meet these targets. The actual amount of these ingredients varies according to the additive technology and to the mineral base stock adopted. Therefore, in principle, it is not possible to give absolute figures. Experience has shown, however, that differences appear in the results of blending studies performed at different locations.

The mineral base stock used is a typical solvent refined SN 150.

The packages selected are commercially available products (A and B with API SJ/CF,

**Table 6** SH Test Program Engine Test Results

| | Oil A | Oil B | SH limits |
|---|---|---|---|
| Sequence II-D | | | |
| Average, merit | 8.6 | 8.5 | 8.5 |
| Sequence III-E | | | |
| Viscosity Increase at 64 h, % | 70 | 93 | 375 max[a] |
| Cam and lifter wear average, μm | 6.8 | 3.2 | 30 max |
| Oil consumption, L | 1.4 | 0.4 | 5.1 max |
| Sequence V-E | | | |
| Average engine sludge, merit | 9.3 | 9.2 | 9.0 min |
| Average engine varnish, merit | 7.2 | 6.8 | 5.0 min |
| Cam wear average, mils | 3.0 | 0.85 | 5.0 max |
| CRC L-38 | | | |
| Bearing weight loss (BWL), mg | 21.0 | 11.6 | 40 max |
| VW GOLF TDI | | | |
| Piston cleanliness, merit | 71 | 73 | 71 |

[a]Previous limit; ACEA A3 current limit is 100 max.

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**Table 7** Composition and Main Characteristics and Sequence V-E Test Results

| | Oil A | Oil B | |
|---|---|---|---|
| PAO 6 cSt | 67.7 | | |
| PIO 6 cSt | | 74.9 | |
| Ester | 15.0 | 8.0 | |
| Package | 12.7 | 12.7 | |
| VI improver (disp. PMA) | 4.6 | 4.4 | |
| Viscosity at 100°C, cSt | 11.84 | 11.85 | |
| Viscosity at −25°C, cP | 3300 | 3300 | |
| **Sequence V-E** | **Oil A** | **Oil B** | **SH/ACEA limits** |
| Average engine sludge, merit | 9.5 | 9.5 | 9 min |
| Rocker arm cover sludge, merit | 9.24 | 9.43 | 7 min |
| Piston skirt varnish, merit | 7.63 | 7.67 | 6 min |
| Average engine varnish, merit | 7.5 | 7.5 | 5 min |
| Oil ring clogging, % | 2 | 1.5 | 15 max |
| Oil screen clogging, % | 2 | 3 | 20 max |
| Stuck compression rings | None | None | None |
| Cam wear average, mils | 0.5 | 1.1[a] | 5 max |
| Cam wear max, mils | 0.5 | 0.5 | 15 max |

[a] Correction factor applied.

ACEA A3/B3 credentials, whereas C is a diesel-oriented technology with ACEA B3/E2 performance). Oil 1 through 4 were intentionally adjusted to tight, borderline rheology to stress possible differences in impact of the two base stocks.

To compensate the small differences in terms of low temperature viscosity between PAO and PIO with the packages A and B, slightly higher amounts on PIO were needed. The engine performance aspect was investigated, too, despite the fact that the current practical approach toward formulation testing and qualification is based on qualification of a fully mineral "core technology." Thus 10W-40, part synthetic formulations (or mineral + NCBO), can be derived without the need of further engine testing on the basis of the BOIG, still retaining all the original qualifications. A performance comparison between part synthetic formulations with PIOs and the same with PAOs (or with NCBOs) could be, therefore, regarded as virtually unnecessary from the point of view of qualifications-related matters, nevertheless still of concern and significant from a "technical" (not to say "academic") point of view.

Tables 5 and 6 report a complete SH program, implemented with a VW GOLF TDI test, carried out to compare engine performance of PIOs and PAOs. The two formulations contain the same amount of hydrocarbon-type synthetic base stock and a small amount of ester. Comparison of the engine test results indicates that PIOs and PAOs, in a given additive system, provide similar performance.

2. Rheological Studies Were Performed

Table 7 reports some significant results relative to SAE 5W-30 formulations. A sequence V-E test, as a key test for API SH/SJ compliance, was then performed on each. This "back-to-back" comparison produced the same "pass" results.

It was then decided not to proceed further with engine test comparison. Indeed, according to the BOI and OEM guidelines, this would involve rerunning all engine tests. Rather, it was

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**Table 8** Composition and Main Characteristics

| Composition (% wt) | SAE 5W-40 oil |
|---|---|
| PIO 4 St | 14.0 |
| PIO 6 cSt | 62.0 |
| Package | 14.0 |
| VI improver (n/d OCP) | 10.0 |
| Main characteristics | |
| Kinematic viscosity at 100°C, cSt | 14.39 |
| Kinematic viscosity at 40°C, cSt | 94.06 |
| Viscosity index | 158 |
| Cold cranking simulator (CCS) dynamic viscosity at −25°C, cP | 3,200 |
| Mini rotary viscometer (MRV) dynamic viscosity at −35, cP | 11,700 |
| Pour point, °C | −45 |
| Viscosity at 150°C, cP at $10^6$ $s^{-1}$ | 4.0 |
| TBN mg KOH/g | 11.0 |
| Sulfated ash, % mass | 1.3 |
| NOACK, % mass | 8.8 |

**Table 9** API SJ Tests Results

| Engine/bench tests results | SAE 5W-40 oil | SJ limits |
|---|---|---|
| Sequence II-D | | |
| Average rust, merit | 8.6 | 8.5 |
| Sequence III-E | | (ACEA A3 limit: |
| Viscosity increase at 64 h, % | 1 (one) | 100 max) |
| Hours to 375% viscosity increase | 85.5 | 64 |
| Cam and lifter wear average, μm | 4.7 | 30 max |
| Oil consumption, L | 1.1 | 5.1 max |
| Sequence V-E | | |
| Average engine sludge, merit | 9.4 | 9.0 min |
| Average engine varnish, merit | 6.6 | 5.0 min |
| Cam wear average, mils | 1.7 | 5.0 max |
| CRC L-38 | | |
| BWL, mg | 10.2 | 40 max |
| Stripped viscosity at 100°C, cSt | 13.77 | 12.5 min |
| Foam tendency, mL | | |
| Stage I | 0/0 | 10/0 |
| Stage II | 0/0 | 50/0 |
| Stage III | 0/0 | 10/0 |
| Stage IV | 120/10 | 200/50 |
| Homogeneity/misc. Federal test method (FTM) 791C | Pass | Pass |
| GM Filterability: GM 9099P | | |
| Flow reduction, % | −3 | 50 max |
| TEOST, mg | 27.8 | 60 max |

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**Table 10** Composition and Main Characteristics

| Formulation and typical figures | Oil A | Oil B |
|---|---|---|
| PAO 6 cSt | 76.4 | 46.3 |
| PIO 6 cSt | | 30.0 |
| Package[a] | 12.6 | 12.7 |
| VI improver (n/d OCP) | 11.0 | 11.0 |
| Viscosity at 100°C, cSt | 14.6 | 15.1 |
| Viscosity at −25°C, cP | 2980 | 3310 |
| Viscosity at 150°C, cP at $10^6$ $s^{-1}$ | 3.9 | 4.0 |
| NOACK, volatility % mass | 8.7 | 8.0 |

[a] Final formulations for both oil A and B involve package at 13.0 wt %.

decided to devote effort to the development of a new formulation (PIO + fully original additive package), in accordance with point 3 listed in Section IV. A.

3. Assessment of Results with PIOs

The API SJ engine tests were successfully completed; ACEA qualification tests are under way. Composition and main characteristics of the formulation are reported in Table 8, and Table 9 gives the API SJ test results.

The formulation exhibits excellent thermal-oxidative stability in terms of Sequence III-E viscosity increase. To obtain further evaluation of the thermal stability properties of PlO-based formulations as well as a more complete comparison with PAOs, double-length III-E tests are scheduled.

4. Assessment of Results of Replacing 30% PAOs by PIOs

The PIO evaluation program was implemented with a fully synthetic formulation obtained replacing 30% of PAO with PIO. According to BOIG, all the original qualifications API SH and ACEA A3/B3 were retained after a Sequence V-E test had been rerun. Composition and Sequence V-E test results are reported in Tables 10 and 11.

## B. Industrial Oils

The field of industrial lubricants, where the final customer, seldom is aware of the costs associated with quality, is more difficult to approach. Some preliminary data in flooded rotary compres-

**Table 11** Sequence V-E Test Results

| Sequence V-E | Oil A | Oil B | SH/ACEA limits |
|---|---|---|---|
| Average engine sludge, merit | 9.4 | 9.41 | 9 min |
| Rocker arm cover sludge, merit | 9.5 | 9.07 | 7 min |
| Piston skirt varnish, merit | 7.8 | 6.65 | 6 min |
| Average engine varnish, merit | 7.0 | 6.04 | 5 min |
| Oil ring clogging, % | 0 | 1.0 | 15 max |
| Oil screen clogging, % | 3 | 0 | 20 max |
| Stuck compression rings | None | None | None |
| Cam wear average, mils | 1.1[a] | 0.67 | 5 max |
| Cam wear max, mils | 0.5 | 2.4 | 15 max |

[a] Correction factor applied.

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**Table 12** Synthetic Compressor Oil ISO VG 46

| Formulations | Oil 1 | Oil 2 |
|---|---|---|
| PIO 6 | 85.5 | |
| PAO 6 | | 85.5 |
| Ester | 12.5 | 12.5 |
| Package rust and oxidation (R&O) + antiwear/extreme pressure | 2.0 | 2.0 |
| Viscosity at 100°C, cSt | 7.3 | 7.3 |
| Viscosity at 40°C, cSt | 42.8 | 42.6 |
| VI | 133 | 137 |
| Neutralization number (NN), mg KOH/g | 0.13 | 0.15 |
| Conradson carbon residue (CCR), % wt | 0.03 | 0.03 |
| Test results | | |
| Rotating compressor oxidation test (ROCOT) | | |
| Evaporative loss, % wt | 0.22 | 0.42 |
| Viscosity increase at 40°C, % | 2.2 | 2.4 |
| DIN 51352 part 2 | | |
| CCR, % wt | 1.91 | 2.13 |
| Evaporative loss, % wt | 9.6 | 9.6 |

sor oil formulations are reported in Table 12, where again PIOs are compared to PAOs. Oxidation stability was determined with the rotating compressor oxidation test (ROCOT) and their overall performance was determined according to a German standard (DIN 51352 part 2).

## V. SUMMARY

PIOs have been extensively tested, in both fully and partly synthetic formulations. This assessment has shown that PIOs can be formulated into top performance lubricants. Compared to PAOs, PIOs offer similar performances in bench and engine tests using the same additive and VII components.

The excellent results obtained in both semisynthetic and synthetic oils, together with a large variety of available raw material make PIOs an interesting new high quality base stock for modern lubricant formulations.

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